# Heat (Enthalpy) of Reaction, Δr*H*

**Enthalpy, *H*,** is a measure of the chemical potential energy stored in the bonds of substances.

A change in enthalpy of a system is equal to the heat released or absorbed at constant pressure.

It is measured in kilojoules, kJ. The change in enthalpy, Δr*H,*

Δr*H* = *Hfinal - Hinitial*

= ∑*Hproducts -* ∑*Hreactants*

**Exothermic and Endothermic processes**

For an exothermic reaction, heat is released and Δr*H < 0 i.e. it has a (-) value.* In this case the products are more stable because they contain less enthalpy than they started with. Note, all combustion reactions are exothermic.

Reactants

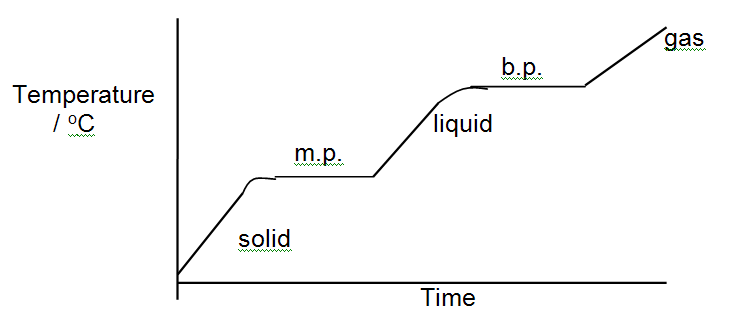
Enthalpy, H Δr*H < 0*

Products

An endothermic reaction absorbs heat from the surroundings because the enthalpy of the products is more than reactants and Δr*H > 0*. This means the temperature of the system gets colder.

*Draw a labelled diagram for an endothermic reaction, showing reactants, products and* Δr*H.*

**Enthalpy of physical changes**

A heating curve of a substance shows the variation of temperature of a sample as it is heated.

At both its melting point and boiling point, even though the sample is being heated, temperature remains constant. All heat being added is used to break the forces holding the molecules in their solid or liquid states, rather than being converted into kinetic energy.

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**Enthalpy of vaporisation, Δ*vapH****,* is the difference in enthalpyper mole of molecules between the vapour and liquid states of a substance.

Δ*vapH = Hvapour - Hliquid*

e.g.H2O(l) 🡺 H2O(g) .

Δ*vapH* (H2O) = +40.7 kJ mol-1

Vaporisation is always endothermic as molecules need energy to overcome the attractive forces holding the molecules in the liquid state. Cooling a gas to a liquid will always be exothermic as heat is released as the bonding forms between molecules in the liquid state.

**The enthalpy of fusion, Δ*fusH****,* is defined as the enthalpy change that occurs when one mole of molecules changes from solid to liquid state.

e.g.H2O(l) 🡺 H2O(g) .

All enthalpies of fusion (**melting**) are positive as energy must be added to cause the molecules to vibrate more vigorously until they can move past each other and flow as a liquid. The enthalpy change for freezing is the negative value of the equivalent enthalpy change of fusion.

# Enthalpy of chemical reaction

Like all hydrocarbons methane undergoes complete combustion to form carbon dioxide and water.

CH4(*g*) + 2O2(*g*) → CO2(*g*) + 2H2O(*l*) Δ*rH0* = -890 kJ mol-1

The enthalpy value given is for the reaction carried out at standard state (one atmosphere pressure). This means that the water produced is in the **liquid** rather than gaseous state. If the water produced were in the gaseous state, then the value of Δ*rH0* would not be the same.

CH4(*g*) + 2O2(*g*) → CO2(*g*) + 2H2O(*g*) Δ*rH0* = -802 kJ mol-1

Note that the unit for Δ*rH0* is kJ mol-1. This refers to the number of moles of reactants and products in the specific balanced equation for which the value of Δ*rH0* is given. It may or may not be 1 mole of each reactant.

For combustion of two moles of CH4(g) then Δ*rH0* = - 1780 kJ mol-1.

Because the **state** of the reactants and products is highly significant in thermochemical equations, it is important that they are always included.

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**Standard enthalpy of combustion, Δ*cH0***

The standard enthalpy of combustion is the change in enthalpy **per one mole** of a substance when it reacts completely with oxygen under standard conditions and the units of Δc*H0* are kJ mol-1.

In the complete combustion of an organic compound the carbon atoms are converted to CO2(*g*) and the hydrogen atoms are converted to H2O(*l*).

Exercise - Write equations for the reactions which have the following enthalpies of combustion:

Δ*cH0* (H2) = -286 kJ mol-1

Δ*cH0* (CH3OH) = -726 kJ mol-1

**Standard enthalpy of formation, Δ*fH0***

Δ*fH0* is the standard reaction enthalpy for the formation of **one mole** of substance from its elements in their most stable form at standard state. The units of Δ*fH0* are kJ mol-1 and the equation it refers to must have only **one mole** of product. e.g.

4C(*s*) + 6H2(*g*) + O2(*g*) → 2C2H5OH (*l*) Δ*rH0*  = -555 kJ mol-1

i.e.Δ*fH0* (C2H5OH, *l*) = -555 ÷ 2

= - 277.5 kJ mol-1

The **standard enthalpy of formation of any element** in its standard state is arbitrarily defined to be **zero** kJ mol-1.

#### Exercise - Write balanced equations for the formation reactions of

1. C6H12O6(s)
2. CO(g)

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

ENERGY CALCULATIONS

**Measuring enthalpies of reaction – calorimetry**

To measure enthalpy changes, the reaction it is carried out in an insulated container (such as a polystyrene cup) and the temperature change is measured. Using this temperature change, ΔT, and the value of the specific heat capacity,( c = 4.18), the amount of energy transferred to the mass *m* of substance can be calculated using the expression

*E = m x* 4.18 *x* ΔT

#### Exercise 25.0 mL of 1.0 mol L-1 HCl is placed in a polystyrene cup and its temperature is measured as

*21.0 oC. Following the addition of 25.0 mL of 1.0 mol L-1 NaOH solution, the mixture is stirred and the final temperature recorded as 27.8 oC. Calculate the molar enthalpy change,* Δ*rH in kJ mol-1,for this reaction*.

**Hess’s Law**

If an overall reaction can be broken down into a series of two or more steps, then the enthalpy of reaction is the sum of the enthalpies of the individual reaction steps. The energy difference depends only on the difference in energy between the reactants and products, not on the reaction path taken.

E.g. the process of photosynthesis is an endothermic process in which energy from the sun is trapped and stored in the bonds of glucose.

6CO2(*g*) + 6H2O(*l*) → C6H12O6(*aq*) + 6O2(*g*) Δr*H0* = **+**2808 kJ mol-1

It is however easier to measure the enthalpy change for the reverse reaction, the combustion of glucose C6H12O6(*aq*) + 6O2(*g*) → 6CO2(*g*) + 6H2O(*l*) Δr*H0* = **-**2808 kJ mol-1

#### Exercise

The octane in petrol may burn to carbon monoxide, CO, if the air supply is limited. Given the standard enthalpies of combustion of C8H18(l) and CO(g),calculatethe standard reaction enthalpy for the incomplete combustion of one mole of octane.

C8H18(l) + 8.5O2(g) → 8CO(g) + 9H2O(l) **1** Δc*H*o (C8H18, l) = -5471 kJ mol-1

Δc*H*o (CO, g) = -283 kJ mol-1

Solution:

Start by writing equations for the two combustion reactions .

C8H18(*l*) + 12.5O2(*g*) → 8CO2(*g*) + 9H2O(*l*) **2**

CO(*g*) + 0.5O2(*g*) → CO2(*g*) **3**

Equation 1 shows that 8 moles of CO are needed as a product, so equation 3 is reversed and multiplied by 8.

8CO2(*g*) → 8CO(*g*) + 4O2(*g*) Δ*rH0* =(+283 x 8) kJ mol-1

Equation 1 also shows that 1 mole of C8H18 is required as a reactant, so this can be added to the equation above to obtain the required overall equation.

8CO2(*g*) → 8CO(*g*) + 4O2(*g*) Δ*rH0* = + 2264 kJ mol-1

C8H18(*l*) + 12.5O2(*g*) → 8CO2(*g*) + 9H2O(*l*) Δ*rH0* = - 5471 kJ mol-1

C8H18(*l*) + 8.5O2(*g*) → 8CO(*g*) + 9H2O(*l*) **Δ*rH0* = -3207 kJ mol-1**

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

#### Exercise

*Calculate the enthalpy change for the formation of ethanol from CH4 according to the equation:*

*2CH4(g) + O2(g)* → *2CH3OH(l)*

*Use the following equations and heats of reaction.*

*CH4(g) + H2O(g)* → *CO(g) + 3H2(g)* Δ*rHo = +206 kJ mol-1*

*2H2(g) + CO(g)* →  *CH3OH* Δ*rHo = -128 kJ mol-1*

*2H2(g) + O2(g)* →  *2H2O(g)* Δ*rHo = -484 kJ mol-1*

**Calculating Δ*rHo* given the standard heats of formation.**

**Δ*rHo*** can be obtained by subtraction of the standard enthalpies of formation of reactants from those of the products.

**Δ*rHo* = ∑ n Δ*fHoproducts -* ∑ n Δ*fHoreactants***

*E.g.* Using the standard heats of formation of CO2(*g*), H2O(*l*), and C6H12O6(*s*), calculate the standard enthalpy of combustion of glucose.

ΔfHo(CO2, *g*) = -394 kJ mol-1

ΔfHo(H2O, *l*) = -286 kJ mol-1

ΔfHo(C6H12O6, *s*) = -1268 kJ mol-1

C6H12O6(*s*) + 6O2(*g*) → 6CO2(*g*) + 6H2O(*l*)

ΔrHo = ∑ nΔfHoproducts - ∑ nΔfHoreactants

ΔrHo  = (6 x -394 + 6 x -286) - (-1268 + 0) = - 2812 kJ mol-1

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

#### Exercise

*1. a) Calculate the enthalpy change for the following reaction.*

*2SO2(g) + O2(g)* →  *2SO3(g)*

*ΔfHo(SO2, g) = -297 kJ mol-1  ΔfHo(SO3, g) = -396 kJ mol-1*

**Using Bond Enthalpies to calculate Δr*Ho***

Bond enthalpy is the change in enthalpy when the covalent bond, **in a gaseous molecule,** is broken. It is always a positive value because bond breaking always requires an input of energy. Also, making bonds releases energy..

The stronger a covalent bond, the higher the value of the bond enthalpy. In a polyatomic molecule, the bond strength between a given pair of atoms varies slightly from one compound to another. Thus in CH4 the value of E(C-H) is the average value for all four C-H bonds.

A multiple bond is always stronger than a single bond because more electrons bind the multiply bonded atoms together. These trends can be clearly identified in the table below showing **average** bond enthalpies.

|  |  |  |
| --- | --- | --- |
| **Bond enthalpy /kJ mol-1** | **Bond enthalpy /kJ mol-1** | **Bond enthalpy /kJ mol-1** |
| H - H 436 | C - H 412 | C = C 612 |
| H - O 463 | C - Cl 338 | C o C 837 |
| H - N 388 | C - F 484 | C = O 743 |
| H - Cl 431 | C - O 360 | O = O 496 |
| H - F 565 | C - C 348 | N ≡ N 944 |
| F - F 158 | O – O 146 |  |
| Cl - Cl 242 |  |  |

It is possible to calculate an approximate Δr*Ho* for any reaction (**provided all products and reactants are in the gas phase)** by calculating the difference between the total bond energies for reactants and products in the equation for the reaction.

**Δr*H0* = ∑ Ereactants - ∑ Eproducts**

Note that in this particular calculation we subtract the total bond energies of the products from the reactants. This is because the bond enthalpy is defined as the energy required to break the bond. It is always an endothermic reaction with a positive (+) bond enthalpy.

#### **Example**

Use the average bond enthalpies given in the previous table to calculate the enthalpy change for the following reaction

CH4(g) + 2F2(g) → CH2F2(g) + 2HF(g)

**HINT**:

(i)Draw the molecules out as expanded structural formulae and clearly identify those bonds that are broken and made.

(ii)Remember that some bonds maybe muliple bonds eg O=O and N≡N

(iii)Remember to allow for the number of moles present eg in 2CO2 there are 4 C=O bonds.



+ 2 F-F → + 2H-F

Δr*Ho* = ∑ Ereactants - ∑ Eproducts

= (4 x EC-H + 2 x EF-F )

- (2 x EC-F + 2 x EC-H + 2 x EH-F)

= 1964 - 2922

= - 958 kJ mol-1

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

*Exercises*

1. *Use the bond enthalpies given on the previous page to calculate the standard enthalpy of combustion of the following molecules in the gas phase.*
2. *H2(g)*
3. *CH3CH3(g)*

*2. Calculate the reaction enthalpy for the following reaction:*

*CH2=CH2(g) + HCl(g)* → *CH3CH2Cl(g)*